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(54) Sealant and adhesive compositions

(57) A sealant composition particularly suitable for vehicle tyres comprises a curable butyl rubber and one or more tackifiers, the tensile strength, elongation and cross-link density of the composition being adjusted to

produce the necessary properties for tyre sealants. The composition may also be adapted for use in adhesive products for use in connection with membrane roofing materials. The composition may also include carbon black, zinc oxide, a sulphur component and a conventional cross-linking agent and activator.

GB 2 123 843 A

Reprinted front page

This print embodies corrections made under Section 117(1) of the Patents Act 1977.

This print takes account of replacement documents later filed to enable the application to comply with the formal requirements of the Patents Rules

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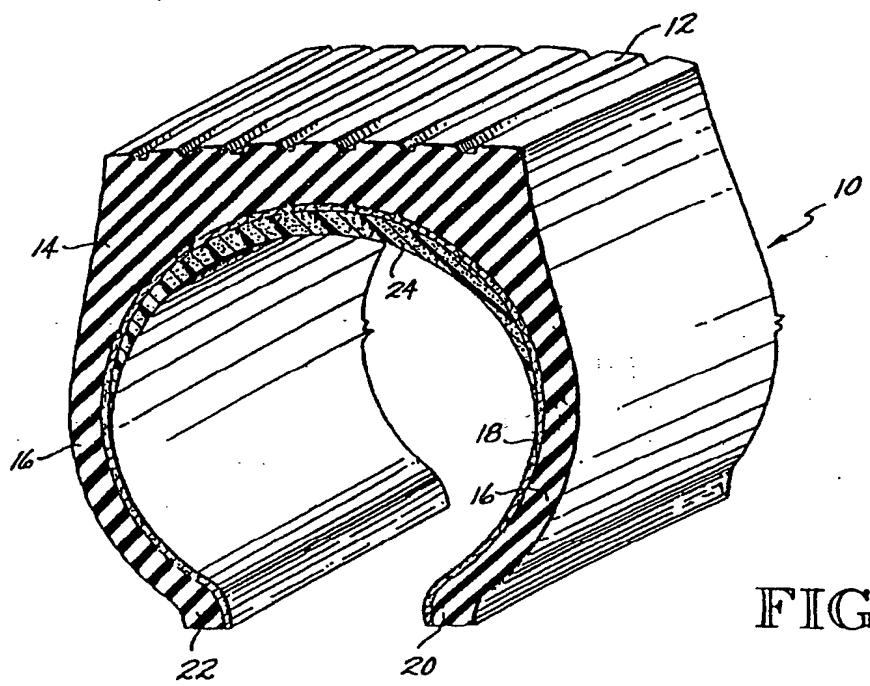


FIG. 1

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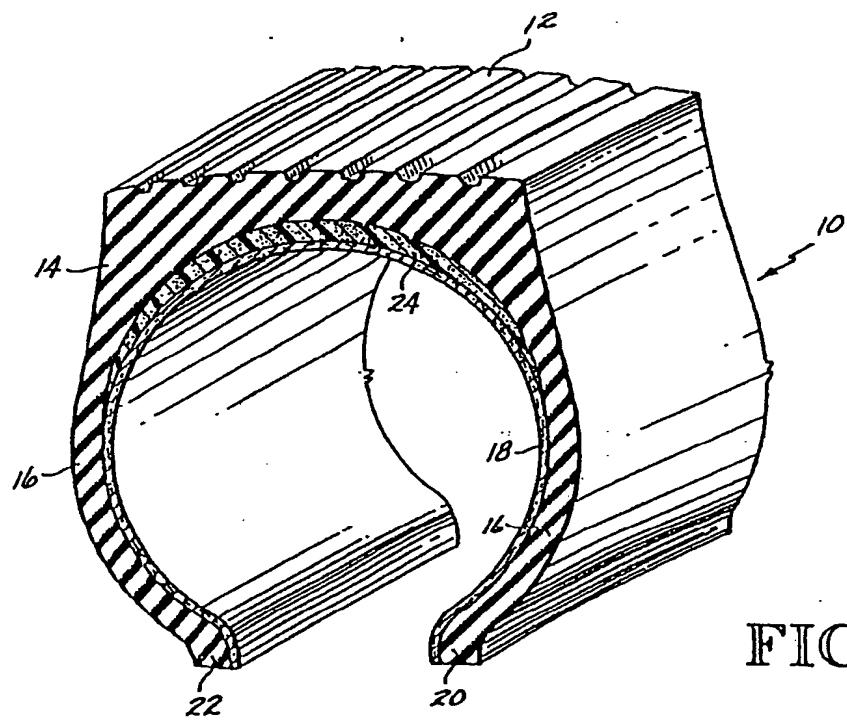


FIG. 2

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FIG. 3

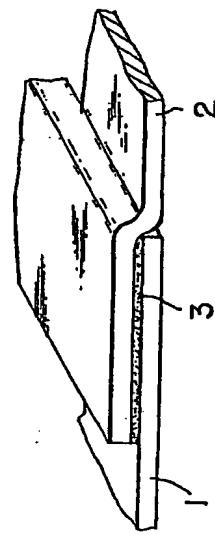
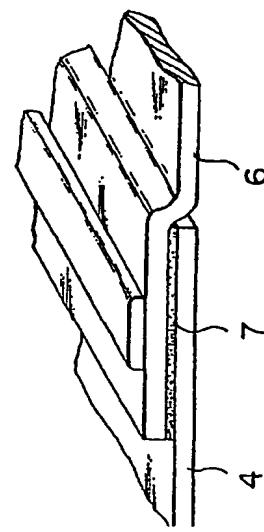


FIG. 4



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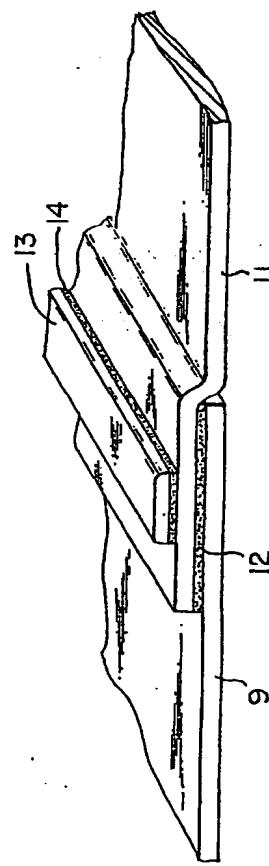


FIG. 5

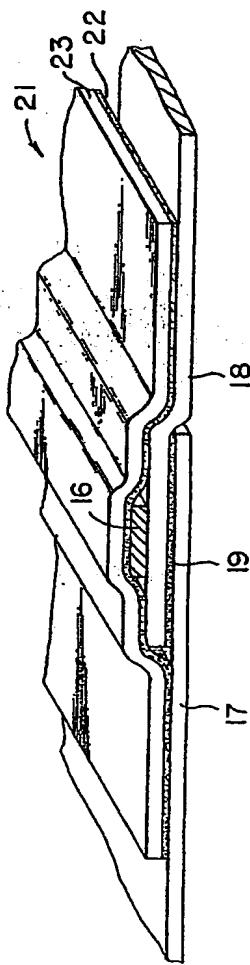
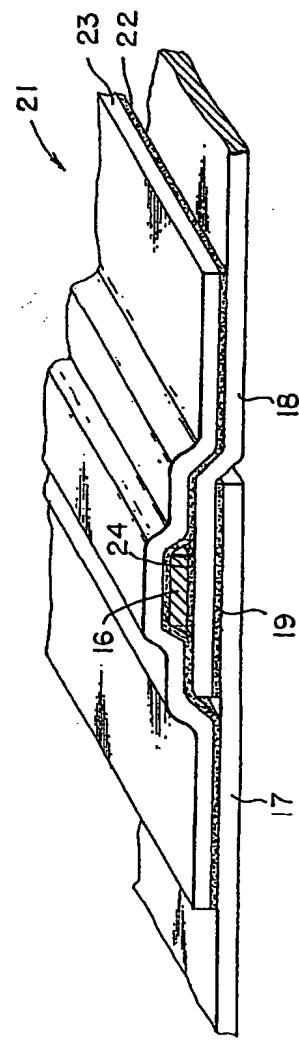


FIG. 6

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FIG. 7



SPECIFICATION
Adhesive composition

Field of the invention

The sealant composition of this invention was developed as a self-healing tire puncture sealant.

5 As a tire sealant, it is adapted for application to the internal surface of a rubber tire and is intended to seal puncture holes in the tread region under widely varying temperature conditions. Being suitable as a tire sealant, the sealant composition of this invention is applicable to other, similar as well as less severe uses.

The composition may also be adapted for use in connection with membrane roofing materials 10 such as EPDM. An adhesive tape compounded according to the invention may be used to splice adjacent sheets of membrane roofing. Additionally, a layer of such adhesive material may be applied to membrane material to make membrane-backed patching and splicing materials. New methods of applying membrane roofing using the tape and patching and splicing materials are described which greatly reduce the time and labor of applying membrane roofing.

15 **Background of the invention**

To be suitable for sealing tire punctures, a sealant composition must meet a unique and exceptionally demanding set of physical and chemical criteria. It must be resistant to aging, decomposition and flow at the high temperatures to which tires are heated under summertime driving conditions. In the case where the puncturing object remains in the tread while the tire continues to be 20 used, the sealant must have sufficient tack and fatigue resistance to remain adhered to the object even as it works back and forth during tire revolution. In the case where the puncturing object is removed from the tread, the sealant must be capable of flowing into the puncture hole at wintertime temperatures and sealing it. Further properties required of a tire sealant are discussed in greater detail below.

25 Because butyl rubber has low air permeability, high resistance to aging and an easily controlled cross-linked density, the prior art has attempted to utilize butyl rubber as a basic compound of tire sealants. One approach, exemplified by U.S. Patents 2,756,801, 2,765,018 and 2,782,829, has been to utilize a single grade of butyl rubber to form the sealant network, and to add tackifiers, plasticizers and other more specialized ingredients such as phenols or iron oxide in an attempt to achieve the 30 necessary balance of physical properties. Compositions based on such patents, however, have not achieved widespread acceptance, primarily because such sealants have failed to perform satisfactorily at the temperature extremes (e.g. -20°F to 220°F) to which tires are subjected.

A second approach to butyl rubber based tire sealants has utilized a combination of high and low 35 molecular weight butyl rubber grades cross-linked together to form a single elastomeric network. Such sealants have been found to perform quite well over wide temperature ranges. However low molecular weight butyl rubber is less readily available commercially than the high weight variety, and sealants based in part on low molecular weight butyl are therefore less attractive.

One of the main difficulties in developing an acceptable tire sealant composition is that a single 40 physical property of such a composition can depend on a great variety of chemical variables. Thus in a sealant composition generally comprising a cured, reinforced butyl rubber and a tackifier, a single property such as tensile strength will depend on the fraction of butyl rubber present, the molecular weight and mole percent unsaturation of the butyl rubber, the amount of cross-linking agent used, the 45 amount of reinforcing agent used, and to a certain extent on the tackifiers and on the curing and application techniques employed. Under these circumstances, it is difficult to specify unique ranges for individual chemical variables, since the overall physical properties of interest depend on the combined effect of many variables. For example it has been found that compositions in which the fraction of butyl rubber present lies within a certain range may be formulated having desirable tensile properties. Yet it 50 may well be possible to reproduce such properties outside such range by adjusting the amount of cross-linking agent used and other variables.

55 In order for a sealant to be practical, it must also be formulated so that it can be easily and practically applied to the tire or article on which it is to be used. One method of applying sealant to the interior of a tire includes the steps of mixing the sealant composition with a curing agent and spraying it into the tire interior as the tire is rotated. Some curing of the sealant occurs as the tire is rotated, resulting in a uniform, seamless coating which resists running and pooling.

55 Solvents such as toluene may be added to the uncured sealant to lower its viscosity in order to facilitate its application. The use of large quantities of solvents in sealant compositions, however, is undesirable. Many solvents which may be used to reduce the sealant viscosity are highly volatile and flammable and therefore present a health and safety risk to workers processing the tires. The expense of the solvents also adds to the cost of the sealant application process.

60 The viscosity of the sealant may also be reduced by heating, although such heating increases the rate of curing, and makes application of the sealant more difficult.

In the field of roofing, increasing use is being made of membrane roofing materials such as EPDM (ethylene propylene diene monomer) and neoprene. Sheets of such materials are generally prepared by

a double calendering process in which two sheets of uncured material are pressed together by rollers to form a single sheet. The composite single sheet is then generally coated with talc, wound into a roll and cured.

Although this calendering process virtually eliminates leakage problems arising from small 5 defects such as pinholes in either of the two original sheets, it increases the cost of the finished product.

The membrane roofing materials are available in sheets of standard widths. Successive sheets of 10 the membrane roofing material are spliced together to form a continuous sheet which covers the roof. Lap joints are typically used to splice adjacent sheets of roofing material. To form such a joint, sheets of 15 the material are positioned adjacent to one another such that they overlap about three inches along the edges to be joined. The edge of the overlying sheet is then folded back such that the contact surfaces of the edges are exposed. The overlapping surfaces are then cleaned with a solvent such as hexane, toluene or white gasoline to remove talc or other foreign material which might impair the strength of the bond. A contact adhesive is then applied to the contact surfaces and allowed to dry. The sheets are 15 then repositioned in overlapping relation and the overlapping areas are pressed together by a roller which is rolled along the joint.

The strength of the lap joint may be improved by use of a primer. Such primer is best applied to 20 the overlapping surfaces of the membrane roofing material after cleaning with solvent but before application of the contact adhesive. The primer may also be used by scrubbing or brushing it onto the overlapping surfaces without cleaning.

This method of joining sheets of roofing material is extremely slow and labor intensive. In addition, the lap joint formed by this method must be sealed with a caulking compound to prevent penetration of moisture along the seam.

An alternate method of joining adjacent sheets of membrane roofing material employs tape 25 composed of a single layer of an uncured elastomeric material which cures in place after application. This tape is applied along the edge of one of the sheets to be joined and the two sheets are then overlapped. A roller is rolled along the joint to press the sheets into engagement with the tape. The tape, however, has a limited shelf life and may even cure before it can be used if left for prolonged periods on a hot roof or in an excessively warm storeroom.

30 Once the sheets of membrane roofing material have been joined to cover the roof, the membrane must be fixed in position. The spliced membrane may be held in position by means of fastening bars which are elongated strips of materials such as plastic or metal. The fastening bars are positioned in the desired location, which may overlay a lap joint, and fastened to the underlying roof structure by fasteners such as screws which extend through the membrane roofing material. In order to prevent 35 moisture seepage, a layer of caulking material is applied to the bottom of the fastening bar prior to fastening it in place, and the heads of the fasteners are caulked after they have been inserted through the fastening bar. Some roofing manufacturers have also attempted to prevent leakage by covering the fastening bar with a strip of membrane roofing material applied with the contact cement and sealed with the roofing caulk as described above with respect to the splicing of the membrane.

40 Emergency repairs of membrane roofing are frequently accomplished by application of a solution of an asphalt-type material. A permanent repair may later be accomplished by removing the patched section of the membrane roofing material and splicing a new piece of material in its place.

Summary of the invention

Applicants have discovered that superior sealant compositions can be formulated by adjusting 45 the compositions so that three key properties are controlled. These three properties are tensile strength, elongation and cross-link density. Tensile strength refers to the maximum stress (force per unit area) that a specimen of sealant material can withstand before rupturing. Elongation measures the relative increase in length of a specimen of material at the point of rupture. Cross-link density is a molecular property which measures the concentration of cross-links present in that part of the sealant 50 which has been cured into a three dimensional cross-linked network. It is most conveniently measured by a swell test which determines the amount of solvent that the three dimensional network present in a given specimen of sealant will absorb.

These three properties—tensile strength, elongation and cross-link density—are important because of their relationship to the properties that a tire sealant must have in order to perform properly. 55 If the tensile strength of a sealant is too low, the sealant will flow under typical tire operating conditions and will also "blow through" a puncture hole when a puncturing object is removed from the tire and fail to seal the hole. An acceptable sealant must therefore be formulated with sufficient tensile strength to withstand such a "blow through".

If the elongation of a sealant is too low, it will have several defects. When an object such as a nail 60 enters tire whose interior is coated with a sealant composition, the sealant should preferably adhere to the nail and form a tent-like structure surrounding it. Adhesion of the sealant to the nail at this time will assist in preserving an air barrier at the puncture and will also result in the sealant being drawn by the nail into the puncture hole as the nail is removed. If the sealant has insufficient elongation, it will be unable to stretch enough to form a tent. The sealant may then "cap" the nail, i.e. a small portion of

sealant surrounding the tip of the nail will break away from the remainder of the sealant and remain adhered to the nail near its tip. Capping generally results in poor nail-in sealing performance. A further result of low elongation will be that in the case of a large puncture, not enough sealant will be able to flow over and into the hole to effect a seal when the puncturing object is removed.

5 The cross-link density of a polymeric sealant determines how strongly the sealant will resist permanent deformation. If the sealant has too high a cross-link density, it will be too resistant to permanent deformation, and the sealant will cap a puncturing object rather than form a tent, with the results described above. If the cross-link density is too low, centrifugal force will cause the sealant to creep or flow at elevated temperatures, resulting in insufficient sealant underlying the shoulder portion 10 of the tire. Too low a cross-link density will also result in a low fatigue resistance for the sealant composition. Fatigue resistance is an important requirement for an effective tire sealant, most particularly in the situation where an object such as a nail enters a tire, and the tire is then used for a considerable time without the nail being removed. In a typical case, of course, a motorist will not even be aware of the nail's presence. Periodic contact between the punctured portion of the tire and the 15 road will result in the nail flexing back and forth as the tire rotates. Assuming that the sealant has formed a tent over the nail, the sealant forming the tent will be continually stretched and relaxed, a process which over time will break cross-links and make the sealant susceptible to flowing away from the nail, thus destroying the air seal.

Sealants according to the present invention comprise cured butyl rubbers present only in the form 20 of a copolymer having a viscosity average molecular weight greater than 100,000, in combination with appropriate tackifiers, in which the tensile strength, elongation and cross-link density of the composition have been adjusted to produce the required sealant characteristics as described above. In general, tensile strength, elongation and cross-link density may most readily be controlled by adjusting the fraction of butyl rubber in the total composition, the amount of cross-linking agent used, the 25 amount of reinforcer used, the molecular weight and degree of mole unsaturation of the butyl rubber, and to a lesser extent the tackifiers and processing methods used. It has been found that preferred sealants for vehicle tires are those in which the tensile strength is in excess of 30 psi, the elongation is in excess of 600%, and the swell ratio in toluene lies between 12 and 40. Furthermore, sealants having elongations in excess of 800% and swell ratios in the range of 12-35 have been found to be 30 particularly suitable as vehicle tire sealants and are especially preferred. Such sealants may be formulated by adjusting the butyl rubber to comprise about 13-40% by weight of the total composition excluding the cross-linking agents, by using a butyl rubber having a mole percent unsaturation between about 0.5 and 2.5 and a molecular weight of about 100,000-450,000, and by using between about 0.5-6 phr of a quinoid cross-linking agent and at least about 2 phr of carbon 35 black. Such sealants having 13-20% butyl rubber, 30-60 phr carbon black and 2-6 phr of a quinoid cross-linking agent are especially preferred because they are readily formulated having properties in the above ranges and because they possess significant processing advantages as described below. Sealants having tensile strengths, elongations, and swell ratios in the ranges set forth above may also be formulated by adjusting the butyl rubber to comprise about 13-50% by weight of 40 the total composition less the cross-linking agents by using a butyl rubber having a mole % unsaturation between about 0.5-2.5 and a molecular weight of about 100,000-450,000, and by using between about 5-25 phr of a bromomethylated phenolic resin curing agent and at least 3 phr of zinc oxide.

Benzoyl peroxide is a preferred oxidizer which may be used as the activator for the cross-linking 45 of the butyl rubber by means of the quinone dioxime curing system. When a sealant composition is processed at elevated temperatures, however, as may be desired to reduce its viscosity, benzoyl peroxide causes extremely rapid cross-linking of the butyl rubber, resulting in an almost immediate gelling of the sealant and making application and handling thereof more difficult. Oxidizing agents of lesser activity, such as t-butyl perbenzoate or other peroxy esters, lead dioxide and diacyl peroxides 50 may be used to increase the curing rate, including the gel time of the sealant composition, but the high temperature stability and hence the resistance to aging of sealant compositions cured with these compounds is reduced. In order to overcome these difficulties, two oxidizing agents capable of activating the cross-linking of the butyl rubber may be used. In such case, one of the components of the activator system should be of relatively higher activity and the second should be of lesser activity. By 55 adjusting the relative concentrations of the two oxidizing agents, the gel time and curing time of the sealant can be controlled to facilitate its application. Zinc oxide and sulfur may be used in combination in the sealant to provide superior high temperature stability and aging characteristics.

The present invention thus provides a sealant which is usable over a wide temperature range, which gels and cures at a rate which can be controlled to facilitate application and handling, and which 60 is particularly resistant to aging. Since the sealant may be compounded according to the present invention so as to permit application and curing at elevated temperatures. The viscosity of the sealant may be reduced by heating, thus reducing or eliminating the need for the addition of solvents.

Although the addition of either zinc oxide or sulfur alone will provide some improvement in the high temperature stability of the sealant compositions, their combined use provides an increase in 65 stability of the sealant which is greater than that expected from their independent use. Preferably,

concentrations of 3% zinc oxide in conjunction with sulfur or a second sulfur constituent are used to improve the high temperature stability of the sealant.

The sealant composition of the present invention may be adapted to function as an adhesive usable in connection with membrane roofing materials. The adhesive composition is compounded in like manner to the sealant composition with the exception that the components are adjusted such that the adhesive has a tensile strength of at least 50 psi, an elongation of at least 600%, a modulus at 300% elongation of less than 12, and a modulus at failure of less than 20. Preferably, however, the adhesive is compounded to have a tensile strength of at least 60 psi, an elongation of at least 800% and preferably more than 1000%, a modulus at 300% elongation of at most 8, and a modulus at failure 10 of at most 16.

The adhesive is used by preparing it as a thin tape composed of adhesive material. Alternately a layer of the adhesive material may be applied to a thin strip of roofing material or other membrane material to form a cover strip in either of these two embodiments, the adhesive layer may be backed with a standard silicone coated release paper and rolled into a roll for transportation or storage. The 15 present invention thus provides an adhesive composition which is easy to transport and store, which has a long shelf life, which is easy to use, and which may be used to form an adhesive tape or two-ply cover strip. In use, the adhesive composition provides an initially strong, water resistant seal between sheets of the membrane roofing material, is usable in a variety of weather conditions, is stable at the elevated temperatures encountered in roofing applications, does not become brittle at low 20 temperatures, and remains sufficiently strong and flexible to withstand the expansion and contraction of the roof. In addition, the present adhesive does not emit solvents during use which may be detrimental to laborers.

Brief description of the drawings

Figure 1 is a perspective view of a cross-section of a vehicle tire illustrating one embodiment of 25 the invention in which the sealant composition layer is located on the innermost surface of the tire behind the tread.

Figure 2 is a perspective view similar to Figure 1, illustrating a second embodiment of the invention in which the subject sealant layer is located behind the tread portion of the vehicle tire and between an air-impervious film conventionally employed in a tubeless tire and the carcass portion of 30 the tire.

Figure 3 is a perspective view of sheets of membrane roofing material which have been spliced using the adhesive tape of the present invention.

Figure 4 is a perspective view of sheets of membrane roofing material which have been spliced using the adhesive tape of the present invention and illustrates one method of using a fastening bar 35 with the present adhesive composition.

Figure 5 is a perspective view of sheets of membrane roofing material which have been spliced using the adhesive tape of the present invention and illustrates another method of using a fastening bar with the present adhesive composition.

Figure 6 is a perspective view of a sheet of membrane roofing material which has been spliced 40 using the adhesive tape of the present invention and illustrates one method of using the two-ply cover strip with a fastening bar.

Figure 7 is a perspective view of a sheet of membrane roofing material which has been spliced using the adhesive tape of the present invention and illustrates another method of using the two-ply cover strip with a fastening bar.

45 Detailed description of the invention

The copolymer network which provides the strength and continuity of the sealant compositions of the present invention is comprised of cured butyl rubber. Butyl rubber is intended to include copolymers of 96—99.5 wt.% isobutylene and 4—0.5 wt.% isoprene (Butyl IIR) as well as other rubbery copolymers of a major proportion (i.e. over 50% by weight) of an isoolefin having from 4 to 7 50 carbon atoms with a minor proportion by weight of an open chain conjugated diolefin having from 4 to 8 carbon atoms. The copolymer may consist of from 70 to 99.5% by weight of an isomonoolefin such as isobutylene or ethyl methyl ethylene copolymerized with from 0.5 to 30% by weight of an open chain conjugated diolefin such as isoprene; butadiene-1,3; piperylene; 2,3-dimethyl-butadiene-1,3; 1,2-dimethyl-butadiene-1,3 (3-methyl pentadiene-1,3); 1,3-dimethyl butadiene-1,3; 1-ethyl butadiene-1,3 55 (hexadiene-1,3); 1,4-dimethyl butadiene-1,3 (hexadiene-2,4); the copolymerization being effected by the usual manner of copolymerizing such monomeric materials. "Butyl rubber" as used herein also includes halogenated butyl rubber, of which chlorobutyl and bromobutyl are the best known varieties. The halogen is generally believed to enter the butyl rubber molecule by substitution at the allylic position in the diolefin unit. Typical chlorobutyl rubbers have about 1.0—1.5 weight per cent chlorine. 60 "Butyl rubber" also includes those varieties of butyl rubber in which conjugated diene functionality has been added in the linear backbone at the diolefin units. Such conjugated diene butyls are described in U.S. Patent 3,816,371.

The sealant compositions of the present invention may be formulated using any of the standard

high molecular weight grades of butyl rubber. Such grades have viscosity average molecular weights in excess of 100,000, and most commonly in the range 300,000—450,000. They are to be distinguished from the low molecular weight butyl grades, which have viscosity average molecular weights on the order of one-tenth of the high weight grades. Sealants of the present invention do not 5 include low molecular weight butyl grades. Representative examples of high weight butyl grades are Butyl 065, Butyl 165, Butyl 268, Butyl 365, Butyl 077, Chlorobutyl 1066 and Chlorobutyl 1068, all available from the Exxon Oil Company, and BUCAR 1000 NS, BUCAR 5000 NS, BUCAR 5000 S and BUCAR 6000 NS, all available from Cities Service Oil Company. While the use of butyl rubber having a molecular weight in excess of about 450,000 will not detract from the sealing qualities of the sealant, 10 such butyl rubber is comparatively difficult to dissolve and combine with other constituents, as well as difficult to apply via an airless spraying technique. Thus the preferred weight range for the high molecular weight butyl rubber is from 100,000 to about 450,000. Furthermore, butyl rubber having molecular weights in the range of 300,000—450,000 have been found particularly useful for formulating sealants having desirable tensile and elongation properties, and are especially preferred. 15 Cross-linking of the butyl rubber may be effected by any of the well-known curing systems, including sulfur and sulfur containing systems, quinoid systems, and phenolic resin systems. For halogenated butyl, additional useable curing agents include primary amines and diamines, secondary diamines, zinc oxide combined with alkyl dithiol carbamates such as tetramethyl thiuram disulfide, and 1,2—1,3 dialkyl thioureas. For butyl containing conjugated diene functionality, additional useable 20 curing agents include poly-functional dieneophiles, such as ethylene glycol dimethacrylate and trimethylol propane trimethacrylate. 20 Although butyl rubber may be cured using a vulcanization process (sulfur and accelerators such as mercaptobenzotiazole), such a cure results in a rubber that over time is subject to degradation caused by oxygen or ultraviolet radiation. Such degradation may be partially prevented through the use 25 of antioxidants, such as diphenyl-p-phenylene-diamine, phenylbeta-naphthylamine and hydroquinone, and antiozonants, such as N,N'-di(2-octyl)-p-phenylenediamine and N-(1-3-demethyl-butyl)-N'-phenyl-p-phenylenediamine. Nevertheless, the characteristics of the resulting sealant change sufficiently over time to make quinoid and phenolic resin curing systems preferable to vulcanization for the tire sealing applications, where the sealant must be capable of lasting years in a harsh 30 environment. 30 Quinoid cures depend on cross-linking through the nitroso groups of aromatic nitroso compounds. In the quinoid curing system, p-quinone dioxime and p,p-di-benzoylquinone dioxime are preferred as the curing agents. Other suitable curing agents include dibenzoyl-p-quinone dioxime, p-dinitroso benzene and N-methyl-N,4-dinitrosoaniline, the latter two being available on a clay base as 35 "polyac" from E. I. duPont de Nemours & Co. and as "Elastopar" from Monsanto Chemical Co., respectively. The cross-linking activators which may be employed in the sealant composition include inorganic peroxides, organic peroxides (including diaryl peroxides, diacyl peroxides and peroxyesters) and polysulfides. Exemplary are lead peroxide, zinc peroxide, barium peroxide, copper peroxide, potassium peroxide, silver peroxide, sodium peroxide, calcium peroxide; metallic peroxyborates, 40 peroxychromates, peroxycolumbates, peroxydicarbonates, peroxydiphosphates, peroxydisulfates, peroxygermanates, peroxymolybdates, peroxynitrates, magnesium peroxide, sodium pyrophosphate peroxide, and the like; the organic peroxides such as lauryl peroxide, benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, t-butyl peroxybenzoate, dibenzoyl peroxide, bis(p-monomethoxy-benzoyl) peroxide, p-monomethoxybenzoyl peroxide bis (p-nitrobenzoyl) peroxide, and phenacyl peroxide; the 45 metallic polysulfides such as calcium polysulfide, sodium polysulfide, potassium polysulfide, barium polysulfide and the like, some sulfur bearing organic compounds such as disclosed in U.S. Patent No. 2,619,481, and the organic polysulfides, which possess the general formula R—(S)_x—R where R is a hydrocarbon group and x is a number from 2 to 4. The actual cross-linking agent is believed to be the oxidation product of quinone dioxime, p-dinitroso benzene. 50 The quinoid curing agent/cross-linking activator combination which has been found to result in the shortest gel time is the p-quinone dioxime/benzoyl peroxide combination. The preferred concentration of p-quinone dioxime is 0.5—6 phr. The preferred concentration of benzoyl peroxide is 1.5—18 phr. Accelerators may be employed as appropriate. For example, cobalt napthenate may be used in combination with t-butyl perbenzoate, and chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone) 55 may be used in combination with t-butyl perbenzoate or benzoyl peroxide. 55 At higher temperatures, however, the use of benzoyl peroxide as the cross-link activator causes extremely rapid gelling of the sealant. The gel time of the sealant which is an important part of the curing rate is the time required for the cross-linking reaction between the butyl rubber and the cross-linking agent to proceed to the point that the sealant has become extremely viscous and no longer 60 flows at a perceptible rate. 60 In order to facilitate application of the sealant it may be desirable to adjust the gel rate by using a less active oxidising agent, such as t-butyl perbenzoate or other peroxy esters, as a part of the curing system. Such oxidizers can be mixed with benzoyl peroxide in varying amounts to adjust the gel time of the sealant and to permit the mixing and application of the sealant at higher temperatures. By adjusting 65 the concentration of these two activators, a relatively short gel time can be obtained without an overly 65

rapid curing of the sealant. This occurs because the benzoyl peroxide initially causes rapid cross-linking under the elevated temperatures, but because of its lowered concentration does not complete the gelling and curing of the sealant. The relatively less active t-butyl perbenzoate then completes the curing over a longer time span. By adjusting the relative concentrations of the two oxidizing agents, the sealant can be compounded to gel at a sufficiently rapid rate to a consistency which prevents running or pooling and yet remain fluid long enough to permit easy application to the article to be coated. 5

The high temperature stability of the sealant composition can be greatly improved by the addition of zinc oxide and sulfur thereto as a part of the curing system. Although sulfur may be used to cure butyl rubber by vulcanization, it does not serve as such in the present invention since the sealant is not heated during the curing process to a temperature sufficient to cause any appreciable sulfur cross-linking. 10

Preferably, the zinc oxide is used in an amount not less than 1% by weight of the sealant composition. As zinc oxide is a suitable filler material, it may be added in any amount greater than the 1% minimum which does not adversely affect the characteristics of the sealant. The sulfur should be 15 added in concentrations not less than 0.5—1.0 parts per 100 parts of butyl rubber. Sulfur-containing compounds may also be used as the sulfur constituent in lieu of or in combination with the sulfur. 15

These sulfur constituents should be used in like concentrations to that suitable for sulfur with adjustments made for their increased molecular weight and the number of sulfur-bearing functional groups per molecule. In addition to sulfur, suitable sulfur compounds which may be used as sulfur 20 constituents of the sealant composition include benzothiazyl disulfide mercaptobenzothiazole and its derivatives and salts, dithiocarbamic acid and its derivatives and salts, tetraethylthiuram disulfide, tetrathiomethylene thiuram monosulfide, zinc dibutylthiocarbamate, tellurium diethylthiocarbamate, dipentamethylene thiuram tetrasulfide, and thioureas. Materials which provide sulfur during the cross-linking or aging processes may also be used. Such compounds include aminodisulfides, such as 25 dimorpholene disulfide, tetramethylthiureum trisulfide and polysulfide, polymeric alkylphenol sulfides of sulfur rank equal to or greater than 3, and alkyl or aryl polysulfides of sulfur rank equal to or greater than 3. In general, vulcanization accelerators and materials which provide sulfur either by themselves or through interaction with other materials are usable as a sulfur constituent of the sealant. 25

The use of zinc oxide, sulfur or a sulfur-bearing compound alone, as described above, will result in 30 the improvement of the high temperature stability of the tire sealant. The combined use of the zinc oxide and sulfur or a sulfur compound, however, results in improvements in the stability which is greater than that expected from the use of zinc oxide, sulfur or a sulfur compound alone. The high temperature stability can be even further improved by use of a second sulfur-containing compound, such as benzothiazyl disulfide in conjunction with sulfur. 30

35 Although discussed herein with respect to peroxide activated cross-linking reactions, it is believed that the use of zinc oxide and sulfur will also improve the stability of sealants prepared using the phenolic resin curing system described herein.

The phenolic resins which may be used as curing agents in this invention include halomethylated alkyl phenolic resins, methylol phenolformaldehyde resins, and related species. Bromomethyl alkyl 40 phenolic resins available from Schenectady Chemicals Inc. under the tradenames CRJ-328 and SP-1056 are suitable. The preferred concentration of phenolic resin is 5—25 phr. Such resins do not require the use of activators. 40

The compositions of the present invention includes one or more tackifying agents which enable the composition to adhere to the tire, to a puncturing object, and to self-heal over a puncture hole after 45 the puncturing object has been removed. In general, any tackifying agent compatible with a butyl rubber system may be used. Such agents include polybutenes, polypropenes, paraffinic oils, petrodatum, phthalates, and a number of resins including polyterpenes, terpenephenoilics, blocked-phenolics, modified rosin and rosin esters, and hydrocarbon resins. Preferred tackifiers are polyisobutylenes and hydrocarbon resins, and particularly combinations thereof. 45

50 The sealant compositions of the present invention may include one or more reinforcing agents or fillers. For compositions cured by a quinoid curing system, one of the reinforcing agents must be finely divided carbon. Carbon, such as carbon black, provides reaction sites for the quinoid curing process, and should comprise at least 2 parts of the sealant by weight for each 100 parts of butyl rubber.

Preferred concentrations of carbon black are 30—60 phr. The substance comprising the remainder of 55 the reinforcing agent may either be carbon black or some other suitable substance selected on the basis of the desired color of the sealant. For compositions cured by a phenolic resin curing agent, one of the reinforcing agents must be at least 3 phr of zinc oxide. The preferred concentration of zinc oxide is 5—30 phr. Carbon black may also be used with compositions cured by means of phenolic resins, but its presence is not required. Other well-known reinforcing agents and fillers for butyl rubbers include 60 aluminum hydrate, lithopone, whiting, clays, hydrated silicas, calcium silicates, silicoaluminates, magnesium oxide, and magnesium carbonate. 60

To aid in maintaining sufficient tackiness and thermal stability at elevated temperatures, the sealant compositions of the present invention may include a thermoplastic and elastomeric partially-hydrogenated block copolymer up to about 10 wt.% of the composition, the block copolymer having a 65 general configuration of A—(B—A)_n wherein prior to hydrogenation each A is a monovinyl arene 65

polymer block and each B is a conjugated diene polymer block. Typical A monomers are styrene, alpha methyl styrene and ring alkylated styrenes. Typical B monomers are butadiene and isoprene. The A blocks make up the end groups and typically comprise about one third of the copolymer by weight, and the B blocks make up the mid groups and the balance of the copolymer. The copolymer is partially hydrogenated so that the conjugated diene block segments are substantially fully saturated. The monovinyl arene polymer block segments are not appreciably saturated. Hydrogenation in this fashion enhances the utility of the block copolymer as an oxidation and high temperature-degradation resistant constituent of the sealant composition. The average molecular weight of the copolymers is in the range of about 60,000 to 400,000. Block copolymers of this type are described in U.S. Patent No. 5 3,595,942. 10

The sealant compositions of the present invention are those comprised of the chemical components described above in which the tensile strength, elongation and cross-link density have been controlled so as to provide the optimum properties for tire sealants. Tensile strength is the stress per unit area that a sample of sealant can withstand before rupturing. As used herein, tensile strength is 15 determined by first curing a sample of the sealant in a thin sheet for 24 hours at room temperature, then at 150°F for another 24 hours, and then at 190°F for 4 hours. Dumbbell shaped specimens of sealant are then cut using ASTM die "D", and the dimensions of the dumbbell-shaped specimen are determined. The specimen is then placed in a conventional Dillon tensile testing apparatus having jaws which grip it at its wider end portions, and the specimen is stretched at a cross-head speed of 10 inches per minute until rupture. The tensile strength is the force at rupture divided by the initial cross 20 sectional area of the narrow portion of the specimen. 20

Elongation, as used herein, is determined by a procedure identical to that for tensile strength. The elongation, expressed as a percentage, is calculated by subtracting the initial length of the specimen from its length at rupture, multiplying by 100, dividing by the initial length, and then if necessary by 25 multiplying the result by a correction factor which compensates for any material which may have been pulled out of the jaws gripping each end of the specimen. The initial and final rupture lengths are determined by measuring the distances between the jaws. Thus the specimen being elongated includes not only the narrow, central portion but also some of the wider end portions of the specimen. 25

The modulus of the sealant at various elongations is also determined by a procedure similar to 30 that for determining tensile strength. The modulus is equal to the force required to stretch the sample to a predetermined elongation divided by the elongation expressed as a decimal ratio rather than as a percentage. The modulus at failure is thus the tensile strength divided by the final elongation. 30

Cross-link density may be measured by performing a swell test on a specimen of the sealant using toluene as a solvent. As is known by those skilled in the art, a swell test provides a reliable and 35 repeatable relative measure of cross-link density. The swell test measures the amount of solvent absorbed by a given amount of cross-linked rubber, and the test results are expressed as a swell ratio of weight of solvent absorbed to weight of cross-linked rubber. The greater the cross-link density of a given specimen of rubber the less the elastomeric network is free to expand by absorbing solvent and the smaller the swell ratio will be. The test herein is performed by weighing a specimen of dry 40 (solventless) sealant, soaking the specimen in toluene for 60-72 hours, removing and weighing the wet specimen, and then drying the specimen at 300°F for 30 minutes and reweighing. The weight of solvent absorbed is the wet weight less the final dry weight. Soaking the specimen in toluene will remove the ingredients which have not been incorporated into the toluene insoluble polymer network, and the specimen after soaking and drying will therefore essentially include the cross-linked rubber and 45 the carbon black or other fillers if present. In the case where the sealant included a tackifier such as polyisobutylene containing functional end groups, a portion of the tackifier will remain incorporated into the network as side chains as well. The quantity of toluene insolubles present can be calculated from the initial pre-soaking weight of the specimen plus its known composition, and these figures can be subtracted from the dry, post-soaking weight to yield the weight of cross-linked rubber. 45

The high temperature stability of the sealant composition is tested by compounding a sample of the compositions and allowing them to cure for 24 hours at 150°F. A portion of each sample is then 50 tested as described above for tensile strength, elongation and modulus. The remainder of the samples is then aged for either 5 hours at 300°F, or for 5 hours at 300°F and 69 hours at 150°F. Alternately, the samples may be cured as above for 24 hours and then heated to 300°F for testing. In such case the 55 samples are periodically inspected for changes in appearance. Changes in the luster of the sample and the disappearance of surface texture, for example, indicate that degradation of the sealant has commenced. Since there is a strong correlation between these visual criteria and the performance of the sealant, the periodic visual inspection of the samples provides a quick, nondestructive method of estimating the high temperature stability and hence resistance to aging of the sealant. 55

The above described tests may readily be carried out by those skilled in the art, and the results of such tests may be used to guide the formulation of sealant composition of the present invention. As 60 previously described, the tensile strength of the sealant must be sufficiently high so that the sealant will not "blow through" a typical puncture hole in the range of tire inflation pressures normally encountered. A reliable guide has been found to be that no more than 1/2 inch of sealant should 65 extrude through a .203 inch diameter hole at 32 psig. The elongation must be sufficiently great so that 65

the sealant will be able to adhere to a puncturing object without capping and be able to flow over and into a puncture hole after the puncturing object is removed. The cross-link density must be sufficiently high such that the sealant will not flow at elevated temperatures (e.g. up to 220°F) or fatigue when a puncturing object is left in the tire during use. The cross-link density must not be so high, however, as 5 to cause capping of the sealant when a puncturing object enters the tire. A reliable guide as to whether the elongation is sufficiently high and the cross-link density is sufficiently low has been found to be an 80% or higher pass rate in the static puncture test described in Example I below.

It has been found by applicants that preferred tire sealant compositions are those having a tensile strength of at least about 30 psi, an elongation of greater than about 600%, and swell ratios of 10 between about 12 and 40. Within these ranges, compositions of the present invention have been found to have good tire sealing properties, both when the puncturing object remains in the tire and when it is removed, over the entire temperature range to which tire sealants are normally subjected. Furthermore, sealant compositions of the present invention having elongations in excess of 800% and swell ratios in the range of 12—35 have been found to be particularly suitable as vehicle tire sealants, 15 and are especially preferred.

Sealants having tensile strengths, elongations and swell ratios within these ranges may be formulated by including in the compositions of the present invention 13—40% by weight of butyl rubber having a molecular weight greater than about 100,000 and a mole % unsaturation of between about 0.5 and 2.5, and by employing at least 2 phr of carbon black and about 0.5—6 phr of a quinoid 20 cross-linking agent. The remainder of such compositions are comprised of appropriate tackifying agents, block copolymers, fillers, pigments, and the like. Compositions having 13—20% butyl rubber have been found to have short gel times and to be readily applicable by spray technique, and are therefore especially preferred. Sealant compositions having tensile strengths, elongations and swell ratios as described above may also be formulated by employing 13—50% by weight of butyl rubber 25 having a molecular weight greater than about 100,000 and a mole % unsaturation of between about 0.5 and 2.5, 5—25 phr of a phenolic resin curing agent, at least 3 phr of zinc oxide, with the remainder of the composition comprising tackifying agents and other modifiers.

The sealant compositions of the present invention may be applied by a variety of means. They may be formulated as sprayable compositions that cure in situ, e.g. on the inner surface of a tire, or as 30 compositions that are first cured in sheet form and then applied. They may also be extruded or brushed onto a substrate. A solvent may be employed in the preparation of the sealant composition. Suitable solvents include hexane, toluene, heptane, naptha, cyclohexanone, trichloroethylene, cyclohexane, methylene chloride, chlorobenzene, ethylene dichloride, 1,1,1-trichloroethane, and tetrahydrofuran, as well as combinations thereof.

35 Each particular sealant application process will tend to place constraints on the composition of the sealant itself. Thus, for example, if the sealant is to be solvated and sprayed directly onto a tire, it is desirable to keep the amount of solvent used to a minimum (e.g. 35% or less), so as to simplify solvent recovery procedures and decrease processing time. At solvent levels of 35% or less, however, it has been found that compositions according to the present invention comprising more than about 20% 40 butyl rubber by weight cannot effectively be sprayed by an airless technique by a single fixed nozzle. In airless spray applications, therefore, compositions comprising 20% or less butyl rubber are preferred. Compositions having greater than 20% butyl rubber may be sprayed by a nozzle which tracks back and forth across the tire tread. Since the use of a mixed oxidizer activator together with zinc oxide and a sulfurous compound permits the use of higher processing temperatures, however, the quantity of 45 solvents added to lower the viscosity of the uncured sealant may be reduced. It has been found, however, that compositions according to the present invention comprising more than about 20% butyl rubber by weight cannot conveniently be sprayed by an airless technique by a single fixed nozzle. Without the use of substantial quantities of solvent in airless spray applications, therefore, compositions comprising 20% or less butyl rubber are preferred. Compositions having greater than 50 20% butyl rubber may be sprayed by a nozzle which tracks back and forth across the tire tread.

A second processing constraint on sealants of the present invention involves cure time. The time required for a given sealant to cure will generally affect throughput regardless of the application process used. It has been found that sealants according to the present invention which are formulated with less than about 2.0 phr of a quinoid cross-linking agent will have gel times which are 55 unacceptable long for many applications. Sealants cured in excess of about 2.0 phr of quinoid cross linking agent are therefore preferred. Such sealants must also, of course, have values of tensile strength, elongation and cross link density as described above. Since it in general has been found that quinoid cured sealants comprised of more than about 20% butyl rubber will not have adequate elongations unless less than about 2.0 phr of cross-linking agent are used, the practical effect is that 60 preferred quinoid cured sealants are those comprised of no more than about 20% butyl rubber by weight.

One critical element of the curing rate is the amount of time required for the sealant to gel. No specific test was performed to measure the gel time of the samples tested. The gel time is merely the time required for the viscosity of the sample to increase due to cross-linking of the butyl rubber to the 65 point that it no longer flows appreciably. As with most chemical reactions, the rate of curing of the

butyl rubber increases with increasing temperature and hence the gel time decreases. At elevated temperatures, the gel time can be so brief that the sealant gels before it can be applied. In such case, the gel time of the sealant may be adjusted by using two activators in curing the sealant composition.

The gel time of the sealant may be adjusted by replacing a portion of the benzoyl peroxide with t-butyl perbenzoate, a peroxide of lesser activity. By adjusting the relative concentrations of the benzoyl peroxide and t-butyl perbenzoate, the gel time can be altered as desired. For example, a sealant composition comprising approximately 15% high molecular weight butyl rubber, 76% tackifiers and 9% fillers, and approximately 4 phr quinoid cross-linking agent, gels almost instantly at 230°F—250°F when benzoyl peroxide is used as the sole activator. When a mixed oxidizer activator comprising benzoyl peroxide and t-butyl perbenzoate in approximately equal proportions is used, however, the sealant composition gels in one to two minutes, allowing sufficient time for application. In both cases, the sealant may be cured by heating to 150°F for 24 hours. At even higher temperatures, the benzoyl peroxide could be replaced by another oxidizing agent less active than the t-butyl perbenzoate or a portion of the benzoyl peroxide and t-butyl perbenzoate could be replaced with such oxidizing agent.

Because the sealant compositions described herein have the unique ability to resist oxidation and to remain stable and effective over a wide temperature range, they have numerous applications, such as caulking compounds and as roofing sealants, in addition to their utility as tire sealants. Because the environments to which a tire sealant is subjected is the most severe, the following examples relate the sealant composition to this environment for purposes of illustration. It will be understood that the ratio of the essential ingredients may be varied within the ranges set forth above and that other compounding materials may be replaced by and/or supplemented with such other materials as may be appropriate to deal with the environment contemplated.

With particular respect to the vehicle tire sealant embodiment and with reference to Figure 1, a vehicle tire 10 conventionally includes a tread portion 12, a carcass portion 14 and side walls 16. In tubeless vehicle tires it is generally desirable to employ a barrier layer or lining 18 which is impermeable to air. The air impermeable lining 18 typically extends over the entire inner surface of the tire 10 from one rim contact portion 20 to the other rim portion 22. In accordance with the embodiment of the present invention illustrated in Figure 1, a sealant layer 24 is placed on the inside of the tire 10 against the air barrier layer 18. The sealant layer 24 is arranged to lie principally behind the tread 12 of the tire 10 so that the sealant layer will principally serve to seal punctures occurring in the tread portion of the tire.

Figure 2 illustrates another embodiment of the present invention wherein a vehicle tire 10 has parts similar to those illustrated in Figure 1, and identified by like numerals. However, in this particular embodiment the sealant layer 24 is located between the carcass portion 14 of the tire 10 and the air impermeable barrier layer 18. The vehicle tire embodiment illustrated in Figure 1 normally occurs when the sealant layer 24 is applied after the tire 10 has been formed and cured. The vehicle tire embodiment illustrated in Figure 2 occurs when the sealant layer 24 is incorporated into tire 10 when the tire 10 is itself being formed and cured. The sealant layer may be formed and cured at the same time the vehicle tire is being manufactured to realize production economies, since the subject sealant layer can be cured at the temperatures, about 350°F, employed in curing the other rubber components of the tire. When this is done, it is possible to locate the sealant layer in either position as depicted by Figures 1 and 2, whereas if the sealant layer is applied after the tire is manufactured, it is only possible to place such a layer inside the air impermeable barrier as illustrated in Figure 1. Finally, it should be noted if layer 24 is intended to cover the entire inner surface of the tire, the air barrier layer 18 may be eliminated entirely from the vehicle tire construction.

The sealant compositions utilized in the following examples were prepared by combining the ingredients listed in Table 1 in the proportions indicated, all proportions being given by dry weight.

Table I

| Ingredient | A | B | C | D | E | F | G | H |
|---------------------------------------|------|-------|-------|-----|-----|-----|-----|----|
| Butyl 165 ¹ | 15 | — | — | 20 | — | 35 | — | 40 |
| Butyl 365 ² | — | 13 | 20 | — | 10 | — | — | — |
| 5 Butyl 065 ³ | — | — | — | — | — | — | 40 | — |
| Vistanex ⁴ | 10 | 9.78 | 8.98 | 10 | 10 | — | — | — |
| H-100 ⁵ | — | 19.55 | 17.97 | — | 20 | — | — | — |
| H-300 ⁶ | 23 | — | — | 15 | — | 22 | 20 | 50 |
| H-1900 ⁷ | 40 | 43 | 35.05 | 40 | 40 | 32 | 29 | — |
| 10 Piccotac ⁸ | 5 | 4.89 | 4.49 | 5 | 5 | — | — | — |
| Zinc Oxide | — | — | — | — | — | 10 | 10 | 10 |
| Carbon Black ⁹ | 7 | 4.89 | 8.98 | 10 | 10 | 1 | 1 | — |
| Block | — | 4.89 | 4.49 | — | 5 | — | — | — |
| Copolymer ¹⁰ | — | — | — | — | — | — | — | — |
| 15 Para Quinone Dioxide ¹¹ | 3.0 | 3.0 | 2.47 | 3.0 | 3.0 | 0.5 | 1.0 | — |
| Benzoyl Peroxide ¹¹ | 11.0 | 9.0 | 7.41 | 9.0 | 9.0 | 1.5 | 3.0 | — |
| CJR-328 ^{11, 12} | — | — | — | — | — | — | — | 15 |

20 ¹ Butyl rubber having a viscosity average molecular weight of 350,000 and a mole % unsaturation (isoprene units/100 monomer units) of 1.2, available from Exxon Oil Company under the trademark "Butyl 165". 20

² A butyl rubber having a viscosity average molecular weight of 350,000 and a mole % unsaturation of 2.0, available from Exxon Oil Company under the trademark "Butyl 365". 25

³ A butyl rubber having a viscosity average molecular weight of 350,000 and a mole % unsaturation of 0.8, available from Exxon Oil Company under the trademark "Butyl 065". 25

⁴ A polyisobutylene having a viscosity average molecular weight of 55,000, available from Exxon Oil Company under the trademark "Vistanex LM-MS".

⁵ A polybutene having an average molecular weight of 920 available from AMOCO under the trademark "H-100". 30

⁶ A polybutene having an average molecular weight of 1290 available from AMOCO under the trademark "H-300". 30

⁷ A polybutene having an average molecular weight of 2300 available from AMOCO under the trademark "H-1900". 35

⁸ A hydrocarbon resin having a softening point of 97°C available from Hercules, Inc. under the trademark "Piccotac B". 35

⁹ A furnace black having a surface area of 235 m²/gm, arithmetic mean particle diameter of 17 millimicrons and a pH of 6.0—9.0 available from Cities Service Oil Company under the trademark "Raven-2000".

¹⁰ A block copolymer having a configuration A—(B—A)₁₋₅. A representing a polystyrene block and B representing a hydrogenated polyisoprene block, the isoprene making up about two-thirds of the compound by weight, and the average molecular weight being between 70,000 and 150,000. The compound is available from the Shell Oil Company under the trademark "Kraton G-6500". 40

¹¹ In parts per 100 parts of butyl rubber. 45

¹² A dibromomethyl octyl phenol having a number average molecular weight of 500 and a bromine content of 28—31%, available from Schenectady Chemicals, Inc. under the trademark "CJR-328". 45

Example 1

A tire sealant was prepared according to the formula of composition A above. The butyl rubber, Vistanex, and Piccotac were solvated and blended in hexane so that the mixture contained about 50% solids by weight. The carbon black and the polybutenes were then added to the previously solvated mixture. The p-quinone dioxide was then blended in cyclohexanone to a dilution of about 50% solids by weight, added to the mixture, and dispersed therein to form a first component comprising about 73% solids by weight. This component has been found to have a shelf life of greater than six months.

For a laboratory analysis, a second component was formed by dissolving the benzoyl peroxide in toluene to a dilution of about 3% solids. First and second components were then combined, poured into molds, and then cured for 24 hours at ambient temperature, followed by 24 hours at 150°F and 4 hours at 190°F. Specimens of the sealant were then tested to determine tensile strength, elongation and swell ratio. Tensile strengths for this sealant were found to lie in the range of 35—45 psi, elongations were in the range of 967—998%, and swell ratios were in the range 17.9—18.5.

60 New JR-78-15 steel belted radial tires were utilized for evaluating the sealant composition on a tire. The tires were first cleaned by scrubbing their interior surfaces with a wire brush and soap 60

solution. The surfaces were then rinsed and dried. A first component as described above was prepared and a second component was prepared by dissolving the benzoyl peroxide in methylene chloride such that the resultant solution was about 16% solids. The first component was then preheated to 260°F, combined with the second component to yield a mixture having about 66% solids, and sprayed at 5 about 500 psig onto the interior surface of a rotating tire. The temperature of the first and second components after mixing was about 210°F. 1200 grams of sealant on a solvent free basis were sprayed onto each tire, the resulting sealant layer being between 0.2 and 0.25 inches thick under the central portion of the tread and 0.15 inches thick at the tire shoulder. After spraying, the tires were continually rotated for about ten minutes until the sealant had cured sufficiently to resist flow. The tires 10 were then unloaded from the applicator apparatus and placed in an oven at 140°F—150°F for 30 minutes. 10

The coated tires were subjected to a series of tests to evaluate the "on-the-tire" effectiveness of the sealant. These tests included a blow through test, a static puncture test, and a dynamometer test. The blow through test was conducted by drilling six holes in the tire (2 at .14 inch diameter, 2 at .187 15 inch diameter, and 2 at .203 inch diameter) and plugging the holes with modeling clay prior to sealant application. After application the plugs were removed from the outside, and the tire was inflated to 32 psig at ambient, 42 psig at 180°F, and 46 psig at 220°F. The sealant was considered acceptable if less than about 1/2 inch of sealant extruded through any hole, and if no loss of air from the tire was detected. 15

20 The static puncture test was run at three different temperatures: -20°F; 70°F; and 180°F. At each temperature, an 8 penny nail (.115 inch diameter) and a 20 penny nail (.180 inch diameter) were inserted in the tire tread in each outside groove and 2 of the center tread grooves. Each nail was deflected 45° in two opposite directions for 1 minute, the nails were removed, and the tire was inflated to 32 psig and tested for leakage. The same procedures were then followed except that the tire was 25 inflated prior to puncturing. Air leaks occurring at any time during this test procedure were recorded. 25

The dynamometer test is perhaps the most comprehensive test of tire sealant performance, because it simulates actual driving conditions. The test was carried out on a dynamometer comprising a pivot arm having means for rotatably mounting a tire, movable contact means underlying the tire for contacting the tire tread and causing the tire to rotate, and loading means for forcing the pivot arms 30 downward such that the tire is loaded at a predetermined amount against the contact means. The tests were conducted at loads equivalent to 100% of the tires' rated loads. After being coated with sealant as described above and mounted in the dynamometer, the tires were inflated to 24 psi and broken in for two hours at a rotation rate equivalent to 55 mph. The pressure was then adjusted to 30 psi, and eight nails were inserted as in the static puncture test except using 16 penny (.145 inch diameter) 35 rather than 20 penny nails. The tire was then run again at 55 mph for ten thousand miles or until the pressure dropped below 20 psi, at which point the responsible nail was determined, the nail pulled and the tire patched if necessary, and the test resumed after adjusting the pressure back to 30 psi. 35

In the blow through test an insignificant amount of sealant was extruded at the holes at ambient temperatures, an average of 1/8 inch extruded at 180°F, and an average of 1/4 inch extruded at 40 220°F. In no cases did the tire lose a measurable amount of air. These test results were good and indicate that the sealant of composition A possesses adequate tensile strength to function as a vehicle tire sealant. 40

In the static puncture test the composition sealed an average of 89% of the puncture holes without significant air leakage. Table II gives a detailed breakdown:

| 45 | Table II | | | | 45 |
|----|---------------|-------------|------|-------|----|
| | Nail diameter | Temperature | | | |
| | | -20°F | 70°F | 180°F | |
| | .115 inches | 93% | 97% | 93% | |
| | .180 inches | 83% | 90% | 77% | |

50 These results show good puncture sealing performance, and demonstrate that the sealant possesses sufficient elongation and sufficiently low cross-link density to enable it to adhere to a puncturing object even when the object is flexed back and forth through an arc of 90°. 50

In the dynamometer test, the average distance logged by a 16 penny nail before leakage occurred was 4100 miles, and the average distance for an 8 penny nail was 8500 miles. These distances are a 55 significant fraction of the lifetime of an average tire. Furthermore, the dynamometer test as conducted herein represents conditions which are harsher than those encountered in average driving, since the test is run at 100% of a tire's rated load. These average mileages, therefore, represent excellent all-around sealant performance. 55

Example II

60 Laboratory specimens of composition A were formulated as in Example I except that 4.5 phr of p-quinone dioxime and 16.5 phr of benzoyl peroxide were used. The resulting sealant has a tensile 60

strength of 37 psi, an elongation of 804%, and a swell ratio of 16.2. Increasing the amount of cross-linking agent as expected increased the cross-link density (decreased the swell ratio) but also decreased the elongation to the lower edge of the most preferred range.

Example III

5 Tire sealants were prepared as in Example I for both laboratory and on-the-tire testing according to the formula of composition B above. Toluene was substituted for hexane to facilitate solvation of the block copolymer. The tensile strength, elongation and swell ratios were found to be 34 psi, 987% and 17.83 respectively. In the blow through test, 1/2 inch extruded at 180°F, whereas at 220°F a leak occurred. These results indicate that the tensile strength of the sealant is near its lower preferred value.

10 In the static puncture test, an average of 98% of all punctures were successfully sealed, indicating that the sealant had good elongation and a cross-link density that was not too high. On the dynamometer, the average mileage for 16 and 8 penny nails was 3200 and 6000 miles respectively.

Example IV

15 Laboratory specimens of composition B were formulated as in Example III except that 5.0 phr of p-quinone dioxime and 15.0 phr of benzoyl peroxide were used. The tensile strength, elongation and swell ratio were found to be 27 psi, 627% and 13.89 respectively. As in Example II, increasing the amount of cross-linking agent increased the cross-link density, but the tensile strength and elongation were simultaneously moved out of their preferred ranges. The low tensile strength of composition B is in general due to the comparatively low amount of butyl rubber present (13%). Examples III and IV

20 Indicate that below this level of butyl rubber, it will be difficult to compensate for the low rubber content by increasing the cross-link density while at the same time retaining the tensile strength and elongation in the preferred ranges.

Example V

25 A tire sealant for laboratory analysis was prepared as in Example III according to the formula of composition C above. The tensile strength, elongation and swell ratio were 71 psi, 538% and 12.71 respectively. These results indicate that the sealant is too inflexible to provide optimum vehicle tire performance, although it would perform satisfactorily in other, less severe environments. Results also indicate that at the level of 20% butyl rubber using a quinoid curing system, an appreciable amount of adjusting of other factors will be required to bring the sealant properties within their preferred ranges.

Example VI

30 Tire sealants were prepared as in Example I for both laboratory and on-the-tire testing according to the formula of composition D above. The tensile strength, elongation and swell ratio were found to be 67 psi, 670% and 11.86 respectively. The elongation was improved as compared to Example V, but the elongation is still outside the most preferred range. A static puncture test was performed on this

35 composition, and results are indicated in Table III with an average of 64% of the punctures being sealed successfully.

Table III
 Temperature

| Nail diameter | Temperature | | | 40 |
|---------------|-------------|------|-------|-----|
| | -20°F | 70°F | 180°F | |
| 40 | .115 inches | 53% | 60% | 87% |
| | .180 inches | 50% | 40% | 87% |

As expected based on the elongation test, the composition had the least difficulty sealing punctures at elevated temperatures.

Example VII

45 Laboratory specimens of composition D were formulated as in Example VI except that 2.0 phr of p-quinone dioxime and 6.0 phr of benzoyl peroxide were used. The resulting sealant had a tensile strength of 68 psi, an elongation of 824% and a swell ratio of 13.29. Decreasing the amount of cross-linking agent has as expected increased the swell ratio and has also increased the elongation to within the most preferred range. This example illustrates that in general for quinoid cured compositions

50 having a comparatively larger amount of butyl rubber a preferred sealant may in many cases be achieved by reducing the cross-link density until adequate elongations are produced.

Example VIII

A tire sealant for laboratory analysis was prepared as in Example III according to the formula of composition E above. The tensile strength, elongation and swell ratio were found to be 14 psi, 754% and 17.69 respectively. The low tensile strength is principally due to the low amount of butyl rubber (10% present).

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Example IX

Laboratory specimens of composition E were formulated as in Example VIII except that 5.0 phr of p-quinone dioxime and 15.0 phr of benzoyl peroxide were used. The resulting sealant had a tensile strength of 16 psi, an elongation of 500% and a swell ratio of 12.4. Increasing the amount of cross-linking agent has reduced the swell ratio but has failed by a large margin to increase the tensile strength to within the preferred range. Further, the elongation has been decreased. This example illustrates that it will be difficult to formulate a preferred vehicle tire sealant using only 10% butyl rubber. However, such sealants may well have uses in other applications, for example, as bicycle tire sealants, caulking compounds and the like. 5

10 Example X

Tire sealants for both laboratory and on-the-tire analyses were prepared using the formula of composition F above. The tensile strength, elongation and swell ratio of the laboratory sample were found to be 51 psi, 1850% and 38.05 respectively. Results of the dynamometer test were average mileage of 3800 miles. However, inspection of the tire interiors during the test indicated that flow of sealant had taken place. Such flow is attributable to the comparatively low cross-link density of this sealant. The most preferred sealants are those having swell ratios from 12—35. 15

Example XI

Tire sealants were prepared as in Example X except that 1.2 phr of p-quinone dioxime and 3.6 phr of benzoyl peroxide were used. The tensile strength, elongation and swell ratio of the sealant were 91 psi, 986% and 16.68 respectively. Increasing the amount of cross-linking agent has increased the tensile strength considerably and has reduced the swell ratio to within the preferred range. 20

Dynamometer tests indicated no flow of this sealant. In general, cross-link density (i.e. swell ratio) will be more sensitive to the amount of cross-linker present in compositions such as composition F which include only small amounts of carbon black. Examples X and XI illustrate that a preferred tire sealant 25 can be formed by using 35% butyl rubber and a quinoid curing system if the amount of cross-linking agent and carbon black are sharply reduced. At p-quinone dioxime levels of less than about 2.0 phr, however, the gel time of the sealant becomes quite long. This can be a critical factor in large scale spray application processes, in which the sprayed tires must be kept in the application apparatus and rotating until the sealant has gelled sufficiently to permit handling without flow. It has been found that 30 a gel time of about ten minutes at 150°F will permit a reasonable sealant application rate. The gel time of the sealants of Examples X and XI were 22 minutes and 12 minutes respectively at 150°F. These times could be reduced by increasing the amount of p-quinone dioxime used, but as indicated by these examples, the result might well be to reduce the elongation outside the preferred range. 30

Example XII

Tire sealants for both laboratory and on-the-tire analyses were prepared as in Example I using the formula of composition G above. The tensile strength, elongation and swell ratio of the laboratory samples were found to be 80 psi, 1197% and 17.54 respectively. The dynamometer tests indicated an average mileage of 3100 miles and no perceptible sealant flow. This example, together with Example XI, illustrates that reducing the mole per cent unsaturation of the butyl rubber produces an effect which 40 is opposite to and may partially cancel an increase in the amount of butyl rubber present. 40

Example XIII

Tire sealants for laboratory analysis were prepared in a manner similar to that of Example I using the formula of composition H above. The first component is prepared without the p-quinone dioxime, and 6 parts by weight of the CRJ-328 are dispersed in one part of toluene to form the second component. The tensile strength, elongation and swell ratio of the laboratory samples were found to be 45 56 psi, 1790% and 31.14 respectively. This example illustrates that preferred tire sealants can readily be prepared using phenolic resin curing systems. 45

Example XIV

Laboratory specimens of composition H were prepared as in Example XIII, except that 20 phr of 50 the CRJ-328 curing agent were used. The tensile strength, elongation and swell ratio were 44 psi, 1191% and 18.07 respectively. As expected, increasing the amount of curing agent has decreased the elongation and the swell ratio, but their values are still within the preferred ranges. 50

Example XV

Laboratory specimens of composition H were prepared as in Example XIV, except that 10 phr of 55 the CRJ-328 curing agent were used. The tensile strength, elongation and swell ratio were 44 psi, 2875% and 35.71 respectively. Decreasing the amount of curing agent used has increased the elongation and swell ratio to such an extent that the latter is no longer within its most preferred range of 12—35. The swell ratio is less than 40, however, and this composition will perform acceptably as a vehicle tire sealant. 55

Having established preferred ranges for the sealant composition, samples of the sealant composition were compounded including approximately 15 per cent butyl rubber, 76 per cent tackifier and 9 per cent filler. In addition, approximately four parts of paraquinone dioxime and 12 parts of the cross-linking activator per hundred parts butyl rubber were also included. As set forth in Table I, varying 5 amounts of zinc oxide, incorporated as a portion of the filler, sulfur and sulfur compounds were incorporated into the sealant composition in order to establish the preferred amounts and ranges of these constituents. The zinc oxide and sulfur constituents do not participate in the cross-linking of the butyl rubber, but rather serve to improve the aging characteristics of the solvent. As such, they may be considered as part of the overall curing system, in addition to the cross-linking agent and activator. 5

Table IV

| Example | ZnO % | S phr | High temp. hrs at 300°F | 24 hours at 150°F | | | +5 hours at 300°F | | | 69 hrs at 150°F and 5 hrs at 300°F | | |
|---------|----------|----------|----------------------------|-------------------|------|------|-------------------|------------------|----------------|---------------------------------------|------|------------------|
| | | | | T* | E** | M*** | M**** | M ₃₀₀ | M _f | T | E | M ₃₀₀ |
| 16 | 0 | 0 | — | 49 | 886 | 2.74 | 5.47 | 31 | 1014 | 1.54 | 3.06 | — |
| 17 | 3 | 0 | — | 45 | 832 | 3.73 | 6.46 | 32 | 943 | 2.44 | 3.42 | — |
| 18 | 0 | 0 | 36 | 40 | 1072 | 1.07 | 3.73 | — | — | 16 | 1282 | 0.88 |
| 19 | 0 | 2 | 40 | 41 | 956 | 1.78 | 4.27 | 31 | 925 | 1.86 | 3.31 | — |
| 20 | 1 | 1 | 60 | 47 | 955 | 2.22 | 4.94 | 30 | 900 | 2.64 | 3.36 | — |
| 21 | 1 | 2 | 96 | 43 | 937 | 3.10 | 4.63 | — | — | — | — | — |
| 22 | 2 | 2 | 96 | 46 | 902 | 3.08 | 6.04 | — | — | — | — | — |
| 23 | 3 | 1 | 96 | 48 | 885 | 2.91 | 6.46 | — | — | — | — | — |
| 24 | 3 | 1.5 | 96 | 47 | 849 | 3.38 | 5.49 | — | — | — | — | — |
| 25 | 3 | 2 | 96 | 46 | 888 | 3.02 | 6.22 | — | — | — | — | — |
| 26 | 3 | 3 | 96+ | 47 | 837 | 3.05 | 5.59 | — | — | — | — | — |

* Tensile strength

**Elongation

***Modulus at 300% elongation

****Modulus at failure

*****Modulus at 300°F

M₃₀₀M_f

Examples XVI and XVII

Samples of the sealant composition were cured using the quinoid cross-linking system with benzoyl peroxide as the sole activator. A similar sample of sealant, using three per cent zinc oxide as part of the filler was also compounded. Both samples were cured for 24 hours at 150°F and were

5 again tested. As shown by the test data in Table IV, the sample incorporating the zinc oxide retained 71 per cent of its tensile strength while the sample compounded without the zinc oxide retained only 63 per cent of its tensile strength at the completion of the aging test. The modulus of the sample without zinc oxide at 300 per cent elongation and at failure also decreased by an even greater amount as compared to the sample incorporating the zinc oxide. The addition of zinc oxide to the sealant

10 composition resulted in an improvement of its high temperature stability. 10

Example XVIII

A second sample of the sealant was compounded using a mixed benzoyl peroxide and t-butyl perbenzoate cross-linking activator. The mixed activator was chosen to facilitate mixing and application of the sealant. This mixed activator, comprising approximately 56 per cent benzoyl peroxide 15 and 44 per cent t-butyl perbenzoate, was used for curing the sealant compositions described in all of the remaining examples. After curing for 24 hours at 150°F, this sample was aged for 69 hours at 150°F and 5 hours at 300°F. At the end of the test, the properties of the sample had deteriorated significantly, the tensile strength having decreased to 40 per cent of that of the originally cured sample. A second sample was heated at 300°F and was determined by inspection to have remained suitable as

20 a sealant for only 36 hours. 20

Example XIX

A sample of sealant was prepared as above with the exception that two parts of sulfur per 100 parts of butyl rubber was added. The sample was capable of withstanding 40 hours at 300°F, an improvement of 11 per cent over the sample of Example B. The addition of sulfur thus resulted in an 25 improvement in high temperature stability over the control. 25

Examples XX through XXVI

More dramatic improvements in the high temperature stability of the sealant composition result from the use of zinc oxide and sulfur in combination. For example, when one phr of sulfur and one per cent zinc oxide were used in the composition, the sealant was capable of withstanding 50 hours at 30 300°F, an improvement of 39 per cent over the control without zinc oxide or sulfur and 25 per cent over the sample incorporating two phr sulfur. The tensile strength, nevertheless, did decrease significantly after five hours at 300°F.

35 Sealants compounded with at least one per cent by weight zinc oxide and 1.5 phr sulfur had an even greater resistance to heat aging, being capable of retaining their sealant properties for 96 hours or more at 300°F.

The tensile strength, elongation and modulus of these sealant samples also remained more nearly constant after aging for 69 hours at 150°F and then for five hours at 300°F. The results of these tests are set forth in Table IV.

Preferred concentrations for zinc oxide and sulfur are three per cent and 1.5—3 phr, respectively. 40 In such concentration, the sulfur does not migrate to the surface of the sample and the properties of the sealant are optimized. 40

Examples XXVII to XXXI

Other tests were made in which various concentrations of benzothiazyl disulfide were used and the high temperature stability evaluated as above. The rest of these tests are summarized in Table V. 45 The high temperature stability of the sealant is markedly improved by use of zinc oxide in combination with two sulfur-containing chemicals. 45

Table V
 Example ZnO S Benzothiazyl High temp.
 % phr disulfide hrs at 300°F

| 50 | Example | ZnO | S | Benzothiazyl | High temp. | 50 |
|----|---------|-----|-----|---------------|--------------|----|
| | | % | phr | disulfide phr | hrs at 300°F | |
| 55 | 30 | 3 | 0.5 | 7 | 127+ | 55 |
| | 31 | 3 | 2 | 7 | 102+ | |
| | 29 | 3 | 0.5 | 4 | 161+ | |
| | 27 | 0 | 0 | 4 | 24—40 | |
| | 28 | 0 | 0.5 | 4 | 24—40 | |
| | 32 | 3 | 0.5 | 0.5 | 50 | |
| | 34 | 1 | 0.5 | 4 | 161 | |
| | 33 | 2 | 0.5 | 2 | 106 | |

Examples XXVII and XXVIII

Addition of four phr of benzothiazyl disulfide to the sealant without the addition of the zinc oxide resulted in a limited improvement in the high temperature stability of the sealant. This sealant withstood 24 to 40 hours of aging at 300°F, which is comparable to the 40 hours withstood by the 5 sulfur-containing sealant of Example 19. Similarly, the addition of .5 phr sulfur and four phr benzothiazyl disulfide to the sealant produced only a limited improvement. The sulfur content of the sealants of Examples 27 and 28 is roughly equivalent to that of Example 19, since the molecular weight of the benzothiazyl disulfide is approximately five times that of sulfur.

Examples XXIX to XXXI

10 When the sealant was compounded as in Example 28 with the addition of three per cent zinc oxide, however, the high temperature stability increased by more than 300 per cent over the control and sealants of Examples 27 and 28. This sealant sample withstood in excess of 161 hours at 300°F. Increasing the concentration of the benzothiazyl disulfide to seven phr, however, decreased the high 15 temperature stability such that the composition could withstand only 127 hours at 300°F. Similarly, an increase of the sulfur concentration to two phr and the benzothiazyl disulfide concentration to seven phr resulted in a further reduction of the high temperature stability of the sealant. This sealant was capable of withstanding approximately 102 hours at 300°F. Although this represents a significant decrease relative to the high temperature stability sealant of Example 29, this sealant was nevertheless capable of withstanding a longer heat aging cycle than the comparable sealants including zinc oxide 20 and a single sulfur constituent.

Example XXXII

Decreasing the concentration of the benzothiazyl disulfide in the sealant also resulted in a 25 decreased high temperature stability. A sealant compounded with three per cent zinc oxide, 0.5 phr sulfur and 0.5 phr benzothiazyl disulfide withstood only 50 hours of exposure to 300°F temperatures. Similarly, reducing the concentration of the benzothiazyl disulfide to two phr and the zinc oxide to three 30 per cent resulted in a decrease in the high temperature stability and hence resistance to aging of the sealant. This composition withstood 106 hours of heat aging. When the zinc oxide concentration was reduced to one per cent, however, and the concentrations of sulfur and benzothiazyl disulfide maintained at 0.5 phr and four phr respectively, the sealant withstood 161 hours of heat aging, comparable to that of the sealant of Example 29.

The sealant composition of the present invention may be adapted to function as an adhesive 35 usable in connection with membrane roofing materials. The adhesive composition is compounded in like manner to the sealant composition with the exception that the components are selected and their concentrations adjusted such that the adhesive has a tensile strength of at least 50 psi, an elongation of at least 600%, a modulus at 300% elongation of less than 12, and a modulus at failure of less than 20. Preferably, however, the adhesive is compounded to have a tensile strength of at least 60 psi, an elongation of at least 800% and preferably more than 1000%, a modulus at 300% elongation of at most 8, and a modulus at failure of at most 16.

If the tensile strength of the adhesive is insufficient, it may be subject to tearing or shearing and 40 may thus fail in use. The limit on the elongation of the adhesive relates to the ability of the adhesive to conform to irregular surfaces, as may be encountered when the adhesive is applied over a lap joint or fastening bar. If the sealant has an inadequate elongation, it may pull away from the irregular surface, resulting in leaking of the roof. The modulus at 300% elongation is a function of the force necessary to stretch the adhesive to an elongation of 300%. As such, if the modulus is too high, very small 45 deflections of the membrane roofing material may generate excessive forces in the adhesive. Adhesives with a high modulus at 300% elongation further may be unable to maintain adhesion over irregular surfaces.

Tensile strength and elongation of the adhesive may be adjusted as described in connection with 50 the examples herein. Generally, changes which affect the tensile strength and elongation also affect the modulus at 300% elongation and the modulus at failure. For example, the tensile strength of the sealant and adhesive described herein may be increased by increasing the cross-link density. A large increase in the cross-link density, however, will increase both the modulus at 300% elongation and the modulus at failure. Changes to the kind and quantity of tackifiers also affect the tensile strength, elongation, modulus at 300% elongation, and modulus at failure as is demonstrated by the examples 55 herein.

In addition to the required tensile strength, elongation, modulus at 300% elongation, and modulus at failure, the adhesive should also be compounded to have a shear strength of greater than 15 psi and a peel strength greater than two pounds per inch at 70°F. The shear strength and peel strength relate to the ability of the adhesive to adhere to an object such as membrane roofing material 60 and are related to the amounts and kinds of tackifiers used.

Preferably, the adhesive composition is formed either as a single ply tape of about 0.03—0.05 inch thickness or as a two ply tape or cover strip comprising a layer of the adhesive composition backed by a sheet of EPDM roofing material or other membrane material. Such membrane material

may be single calandered, of course, since the adhesive layer will seal any pinholes or other minor defects therein. In either of these configurations, the adhesive layer may be backed with a standard silicone coated release paper and rolled into a roll for transportation or storage.

The adhesive composition of the present invention is compounded to include butyl rubber, a cross-linking system for the butyl rubber, one or more tackifiers, and one or more fillers in like amounts to those used in compounding the sealant composition described herein. The adhesive composition may also include zinc oxide, sulfur, and/or another sulfur constituent such as benzothiazyl disulfide for improving the high temperature stability and aging characteristics of the adhesive as described above with respect to the sealant. The composition may also contain a plasticizer such as dioctyl azelate. 5

10 The adhesive composition of the present invention may be formulated using readily available standard grades of a butyl rubber such as those described in connection with the sealant composition. As with the sealant composition, the butyl rubber preferably comprises 13—50% by weight of the adhesive composition. When a quinoid cross-linking system is used, however, the butyl rubber most advantageously comprises 13—40% by weight of the adhesive composition exclusive of cross-linking 15 agents, activators and sulfur constituents.

15 The butyl rubber may be cross-linked by any of the well known curing systems but preferably either a quinoid or phenolic resin curing system is used. As with the sealant composition, the preferred quinoid cross-linking agent is p-quinone dioxime. This cross-linking agent is preferably used in connection with a cross-link activator such as benzoyl peroxide or t-butyl perbenzoate. The benzoyl 20 peroxide and t-butyl perbenzoate may, of course, be used in combination to control the gelling and curing rate of the adhesive composition as described herein. Preferably, when a quinoid cross-linking system is used, at least two parts carbon black per 100 parts butyl rubber are included in the adhesive composition.

25 The phenolic resin curing agents discussed with respect to the sealant composition may also be used for cross-linking the butyl rubber. When such cross-linking agents are used, at least three parts of zinc oxide per hundred parts of butyl rubber should be included in the adhesive composition. The preferred concentration of such resins is 5—25 parts per hundred parts butyl rubber.

30 In addition to these constituents, the adhesive composition also includes one or more tackifier agents which enable the composition to adhere to the roofing material, fastening bars, and other objects with which it comes in contact. The kind and quantity of tackifiers used should be chosen to provide adequate adhesion and plasticity across the anticipated range of temperatures to which the adhesive will be exposed. Of the preferred tackifiers listed with respect to the sealant composition, the polybutene sold under the trademark H-300 by AMOCO and the phenolic tackifier sold by Schenectady Chemicals, Inc. under the trademark SP 1068 are especially preferred. In addition, the adhesive 35 composition may include zinc oxide and one or more sulfur compounds for improving the resistance of the adhesive to high temperature.

35 The adhesive composition also includes one or more fillers as described with respect to the sealant composition. If carbon black or zinc oxide is used in connection with a quinoid or phenolic resin curing system, or for improving high temperature stability, such carbon black or zinc oxide may form a 40 part of the filler material.

40 The adhesive compositions of the present invention are those comprised of the chemical components described above in which the tensile strength, elongation, modulus at 300% elongation and modulus at failure have been controlled so as to provide the optimum properties. The composition should also be sufficiently adhesive to the membrane roofing material and other materials as 45 determined by shear and peel tests. The tests of tensile strength, elongation and modulus are performed as set forth with respect to the sealant composition.

45 The shear strength of the adhesive is determined by a procedure similar to that for testing tensile strength. Two 1-inch by 2-inch pieces of membrane roofing material are prepared and are cleaned and/or primed if desired. A 1-inch by 1-inch piece of sealant is then applied to one end of a first piece 50 of the membrane roofing material, and the second piece of membrane roofing material is aligned axially with the first piece and applied to overlap only that portion of the first piece which is covered by sealant. A lap joint is thus formed with the one square inch of sealant disposed between the two pieces of membrane roofing material. Uncoated ends of the membrane roofing material extend in opposite directions from the lap joint.

55 In order to ensure that the adhesive is bonded to the strips, a hand roller is then passed over the lap joint ten times. The free ends of the strips are gripped in the jaws of a tensile strength testing apparatus and pulled apart at the rate of two inches per minute. The force applied to the test sample during the spreading process is monitored and the force at rupture of the sample is the shear strength.

60 The peel strength is determined by a similar procedure. Two 1-inch by 3-inch pieces of EPDM or other membrane roofing material are prepared, and a 1-inch by 2-inch sample of the adhesive is applied to one end of the first strip. The second strip is then positioned directly above the first strip and a hand roller is passed over the sample ten times, using hand pressure, to ensure that the strips and adhesive are completely bonded. The free ends of the strips of membrane material, which extend from the same end of the sample are gripped in the jaws of the tensile strength testing apparatus and pulled 65 apart at the rate of two inches per minute. The force applied to the sample is monitored until the

sample has been completely peeled apart. The peel strength is the average force applied to the sample during the peeling process.

The adhesive composition of the present invention may be used in a variety of ways in connection with membrane roofing material. Figure 3 illustrates a lap joint formed between two parallel sheets of such material 1, 2. To form this lap joint, the sheets of membrane roofing material are laid out parallel to one another with their adjacent edges overlapping approximately two to four inches. The upper sheet 2 is then folded back so that it no longer overlaps the first sheet and the overlapping edges are cleaned and primed if desired. Solvents such as hexane, toluene or white gasoline may be used for cleaning the sheets of membrane roofing material 1, 2. Generally, the sheets of membrane roofing

material are approximately 0.04—0.06 inches in thickness. A tape comprising a single layer of the adhesive material, which is preferably about .03 to .05 inches in thickness, is then applied along the edge of one of the sheets 1, 2. If the adhesive tape has been supplied in roll form with the adhesive composition backed by a release paper, the adhesive material 3 may be rolled onto the edge of one of the sheets 1, 2 as the backing paper is removed. The upper sheet 2 is then folded back into overlapping relation with the lower sheet 1 and a roller passed along the lap joint to ensure a good bond between the two sheets 1, 2 and the adhesive 3. Alternately, the tape could be applied, for example, to the lower sheet 1 with the backing paper adhered to its upper surface. The upper sheet 2 can then be folded back into overlapping relation and the two sheets 1, 2 and adhesive 3 pressed into engagement with a roller as the backing paper is peeled from the upper surface of the adhesive tape 3.

Figure 4 illustrates the use of another method of the adhesive tape of the present invention. As described above, once membrane roofing material has been spliced, fastening bars are used to maintain the spliced sheet of membrane roofing material in position on the roof. According to this method, a lap joint is formed between two adjacent sheets of membrane roofing material 4, 6. A layer of adhesive tape 7 is used to join these sheets 4, 6 to one another as described in connection with Figure 3. A fastening bar 8 is then positioned along the lapped joint so that it overlies the layer of adhesive material 7. Fasteners such as nails or screws are then extended through the fastening bar 8 and overlapping sheets 4, 6 into the underlying roof structure. The layer of adhesive tape 7 serves not only to bond the two sheets of roofing material 4, 6 together, but also to seal the holes made by the fasteners.

Figures 5 and 6 depict two additional methods of fastening joined sheets of membrane roofing material to the underlying roof structure. According to this method, a lap joint is formed between overlapping sheets of membrane roofing material 9, 11 by a layer of adhesive tape 12 as described in connection with Figure 3. A fastening bar 13 is then positioned along the lap joint with a layer of adhesive material 14 disposed between it and the upper surface of the overlapping sheet of membrane roofing material 11. Fasteners driven through the fastening bar into the underlying roof structure must thus pass through two layers of the adhesive material 12, 14 further reducing the likelihood of moisture penetrating through the holes made by the fasteners.

The method illustrated in Figure 6 provides an even greater barrier to penetration of moisture. As in the embodiment of Figure 4, a fastening bar 16 is positioned atop a lap joint formed by two sheets 17, 18 of membrane roofing material and a layer of adhesive tape 19. Fasteners are extended through the fastening bar 16, the two sheets 17, 18 and the adhesive tape 19 and into the underlying roof structure. A cover strip 21, comprising a layer of the adhesive composition 22 applied to a strip of the membrane roofing material 23 is then used to cover the fastening bar and the joint between the two sheets of membrane roofing material 17, 18. The method illustrated by Figure 7 is identical to that of Figure 6 with the exception that a layer of adhesive tape 24 is interposed between the fastening bar 13 and the upper sheets of membrane roofing material 12.

It will be apparent to those skilled in the art that the adhesive composition and adhesive tape described herein may be used equally for applying new roofing and for repairing existing roof structures.

The adhesive compositions of the following examples were prepared by combining the ingredients listed in Table IV in the proportions indicated, all proportions being given by dry weight unless otherwise indicated.

Table IV

| | I | J | K | L | M | N | O | |
|------------------------------|----|----|----|----|----|----|-----|----|
| Butyl Rubber ¹ | 35 | 35 | 35 | 35 | 35 | 35 | 35 | |
| Piccotac | 5 | 5 | — | — | — | — | — | |
| 5 H-300 | 49 | 44 | 54 | 49 | 46 | 54 | 54 | 5 |
| SP 1068 ² | — | — | — | 5 | 5 | — | — | |
| Diethyl Azelate | — | 5 | — | — | 3 | — | — | |
| Carbon Black | 2 | 2 | 2 | 2 | 2 | 2 | 2 | |
| ZnO | 9 | 9 | 9 | 9 | 9 | 9 | 9 | |
| 10 S (phr) | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 10 |
| Benzothiazyl disulfide (phr) | — | 2 | — | 3 | 5 | — | 5 | |
| Para-Quinone Dioxime (phr) | 2 | 2 | 2 | 2 | 2 | 2 | 1 | |
| 15 Benzoyl Peroxide (phr) | — | — | — | 6 | 6 | 3 | 1.5 | 15 |
| T-Butyl Perbenzoate (phr) | 12 | 12 | 12 | — | — | — | — | |

¹The butyl rubber used was a mixture composed of 69% Butyl 165 and 31% Butyl 365.

²⁰SP 1068 is a phenolic thermoplastic tackifier sold by Schenectady Chemicals, Inc.

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Examples XXXIII—XXXV

Samples of the adhesive composition were prepared according to Formulas I, J and K of Table VI. Adhesive tape of 0.05 inch thickness was prepared from each of these samples and cured at ambient temperature for one day and at 158°F for one day. The samples were then tested at ambient

25 temperature for tensile strength, elongation, modulus at 300% elongation, modulus at failure, and shear and peel strength. EPDM sheeting was used in testing the peel and shear strengths of samples of examples 33—35. Since the EPDM material used in the test was relatively clean, hexane cleaning was deemed unnecessary for purposes of the test. All other samples, however, were applied to EPDM sheeting which had been cleaned with hexane. The shear and peel tests were also performed after 30 treating the EPDM membrane with primer. The results of these tests are set forth in Table VII. The peel strength of the samples is given in pounds per inch and the shear strength in pounds per square inch.

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Table VII

| Example | T | E | M ₃₀₀ | M _t | Unprimed | | Primed | |
|---------|----|----|------------------|----------------|----------|-------|--------|-------|
| | | | | | Peel | Shear | Peel | Shear |
| 35 | 33 | 62 | 1719 | 2.05 | 3.58 | 5.0 | 15.4 | 9.5 |
| | 34 | 56 | 1396 | 2.13 | 4.00 | 3.1 | 14.4 | 9.0 |
| | 35 | 67 | 1312 | 2.54 | 5.08 | 3.4 | 14.5 | 9.0 |
| | | | | | | | | 41 |

The samples of examples 34 and of these examples had lower than normal values for shear and 40 peel strength. The EPDM membrane used for testing the peel and shear strengths, however, was not cleaned prior to application of the adhesive composition and thus the lower values are expected. The testing of these three samples also demonstrates the benefits of priming the EPDM roofing material. The primer, distributed by Hughson Chemicals, Lord Corporation, under the trademark TS 3320—19 was diluted to 20% strength by weight with hexane prior to use. The resultant increases in both the shear and peel strengths of the adhesive were quite significant.

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45 It should be noted that adjustments made to the kinds and quantities of tackifiers and plasticizers used in the sealant resulted in changes in the physical properties of the sealant. For example, the formulations I and K differ only in that formulation K contains an additional five parts of polybutene in lieu of the five parts of Piccotac used in formulation I. As a result, the tensile strength of the sample of Example 35 was greater than that of Example 33, and elongation of the sample of Example 35 was less 50 than that of sample 33. Of course, such an increase in the tensile strength and decrease in elongation resulted in an increase in both the modulus at 300% elongation and the modulus at failure.

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Example XXXVI

A sample was prepared according to Formulation L of Table VI in a layer of 0.05 inch thickness and cured at 158°F for one day. This example differs from the previous examples in its use of the tackifier 55 SP 1068 and in its use of benzoyl peroxide as the curing agent. This sample had a tensile strength of 99, an elongation of 1333, a modulus at 300% elongation of 5.74, and a modulus at failure of 7.40. The peel strength of the sample was 7.5 pounds per inch, and the shear strength 33.5 pounds per

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square inch at ambient temperature when applied to hexane cleaned but unprimed membrane. This formulation thus satisfies the criteria for an acceptable adhesive composition.

Example XXXVII

A sample of the adhesive composition was compounded according to formulation M of Table VI and prepared and cured as was the adhesive tape of Example XXXVI. The formulation of the tape of this example differs from that of the preceding example in that a small amount of the polybutene tackifier has been replaced by an equal amount of dioctyl azelate. In addition, the amount of benzothiazyl disulfide has been increased. The tensile strength of this sample was 82 psi, the elongation was 1180%, the modulus at 300% elongation was 7.40, and the modulus at failure was 5 7.06. The peel strength of the adhesive tape was 7 psi, and the shear strength 30.5 psi when applied to hexane cleaned but unprimed membrane. As with Examples 33 and 36, the replacement of polyisobutylene with dioctyl azelate has been accompanied by decreases in the tensile strength and elongation, as well as in peel and shear strength. The physical properties are within the preferred 10 ranges and as such the adhesive of this example would function acceptably.

15 Example XXXVIII

An adhesive tape was prepared in accordance with the preceding two examples using formulation N of Table VI. This formulation does not include the SP 1068 tackifier, but rather uses an increased amount of polybutene tackifier. The tensile strength of the sample was 139 psi, the elongation 973%, the modulus at 300% elongation was 5.60, and the modulus at failure 14.3. The 15 peel strength of the adhesive was 4 pounds per inch, and the shear strength 25 pounds per inch when applied to hexane cleaned but unprimed membrane. Again, an acceptable adhesive composition may be prepared as per this sample, even though the elongation is below the most preferred value. 20

Example XXXIX

An adhesive tape was prepared as in the preceding three examples using formulation O of Table 25 VI. This adhesive composition differs from that of Example 38 in that it includes only half the cross-linking agent and cross-link activator. As a result, this sample is not as highly cross-linked as the sample of Example 38. Accordingly, the tensile strength is only 61 psi, and the elongation has increased to 1515%. The modulus at 300% elongation declined to 2.02, and the modulus at failure to 3.99. The peel strength of the sample was 5.3 pounds per inch, and the shear strength 16.18 psi when 30 applied to hexane cleaned but unprimed membrane.

It will be understood that the invention may be embodied in other specific forms without departing from the spirit of central characteristics thereof. The present examples and embodiments, therefore, are to be considered in all respects as illustrative and not restrictive, and the invention is not to be limited to the details thereof but may be modified within the scope of the appended claims. 30

35 Claims

1. A butyl rubber sealant composition comprising the reaction product of:
butyl rubber;
a cross-linking agent for the butyl rubber;
a cross-linking activator for activating cross-linking of the butyl rubber;
40 at least one tackifier compatible with the butyl rubber;
at least two parts carbon black per hundred parts butyl rubber;
zinc oxide; and
a sulfur constituent.
2. The sealant composition of claim 1 wherein the butyl rubber comprises between 13 and 40%
45 of the sealant composition exclusive of the cross-linking agent, activators and sulfur constituent and wherein the cross-linking agent is a quinoid cross-linking agent present in an amount between about 2-6 parts by weight per hundred parts of butyl rubber.
3. The sealant composition of claim 2 further comprising a second sulfur constituent.
4. The sealant composition of claim 3 wherein the first sulfur constituent comprises sulfur
50 present in an amount not less than 0.5 parts by weight per hundred parts butyl rubber, and wherein the second sulfur constituent comprises benzothiazyl disulfide present in an amount not less than 2 parts per hundred parts butyl rubber.
5. The sealant composition of claim 4 wherein the sulfur constituent comprises sulfur present in an amount not less than 0.5 parts per hundred parts butyl rubber and wherein the zinc oxide comprises
55 at least 1% of the sealant composition.
6. The sealant composition of claim 1 wherein the cross-linking agent is a quinoid cross-linking agent and wherein the sealant composition further comprises first and second activators for promoting cross-linking of the butyl rubber. The second activator having a lower activity than that of the first activator.
60 7. The sealant composition of claim 6 wherein the first and second activating agents are benzoyl peroxide and t-butylperbenzoate. 60

8. A butyl rubber sealant composition comprising the reaction product of:
 butyl rubber;
 a quinoid cross-linking agent;
 a cross-linking activator including first and second activating agents, the second activating agent
 5 having a relatively lower activity than that of the first activating agent for activating cross-linking of the butyl rubber;
 at least one tackifier compatible with the butyl rubber; and
 at least two parts carbon black per hundred parts butyl rubber.

9. The sealant composition of claim 8 wherein the butyl rubber comprises between 13 and 40%
 10 of the sealant composition exclusive of the cross-linking agent, activators and any sulfur constituent, and wherein the quinoid cross-linking agent is present in an amount between about 2—6 parts by weight per hundred parts of butyl rubber.

10. The sealant composition of claim 9 further comprising at least 1% by weight zinc oxide and at least 0.5 parts by weight of a sulfur constituent per hundred parts butyl rubber.

15 11. A membrane roofing adhesive composition comprising the reaction product of butyl rubber, a cross-linking system for said butyl rubber, and a tackifier compatible with butyl rubber, the concentrations of said constituents being chosen such that said adhesive composition has a tensile strength of at least 50 psi, an elongation of at least 600%, a modulus at 300% elongation of not more than 12, and a modulus at failure of not more than 20.

20 12. The adhesive composition of claim 11 wherein the concentration of the constituents is chosen such that adhering composition has a tensile strength of at least 60 psi, an elongation of at least 800%, a modulus at 300% elongation of not more than 8, a modulus at failure of not more than 16 a shear strength of at least 15 psi, and a peel strength of at least 2 pounds per inch.

13. The adhesive composition of claim 12 further comprising zinc oxide and a sulfur constituent.

25 14. The adhesive composition of claim 12 wherein the cross-linking system comprises a quinoid cross-linking agent and an activator for said cross-linking agent and wherein the butyl rubber comprises 13—40% by weight of the adhesive exclusive of the cross-linking system and any sulfur constituent.

15. The adhesive composition of claim 12 wherein the cross-linking system includes 5—25 parts
 30 of a phenolic cross-linking agent per hundred parts butyl rubber.

16. A membrane roofing adhesive tape comprising a layer of adhesive material, the adhesive material comprising the reaction product of butyl rubber, a cross-linking system for the butyl rubber, a tackifier compatible with butyl rubber and a filler material, the concentrations of the constituents being chosen such that the adhesive composition has a tensile strength of at least 50 psi, an elongation of at least 600%, a modulus at 300% elongation of not more than 12, a modulus at failure of not more than 20, a shear strength of at least 15 psi and a peel strength of at least 2 pounds per inch.

35 17. The adhesive tape of claim 16 further comprising zinc oxide and a sulfur constituent whereby the stability of the adhesive is improved.

18. The adhesive tape of claim 16 wherein said tape further comprises a layer of flexible
 40 membrane adhered to one side of the layer of adhesive composition.

19. A sealant composition substantially as herein described.

20. A membrane roofing adhesive composition substantially as herein described.

21. A membrane adhesive roofing tape substantially as herein described.